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Process Emission Initiatives by the Society of the Plastics Industry, Inc.

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Outline of Contents

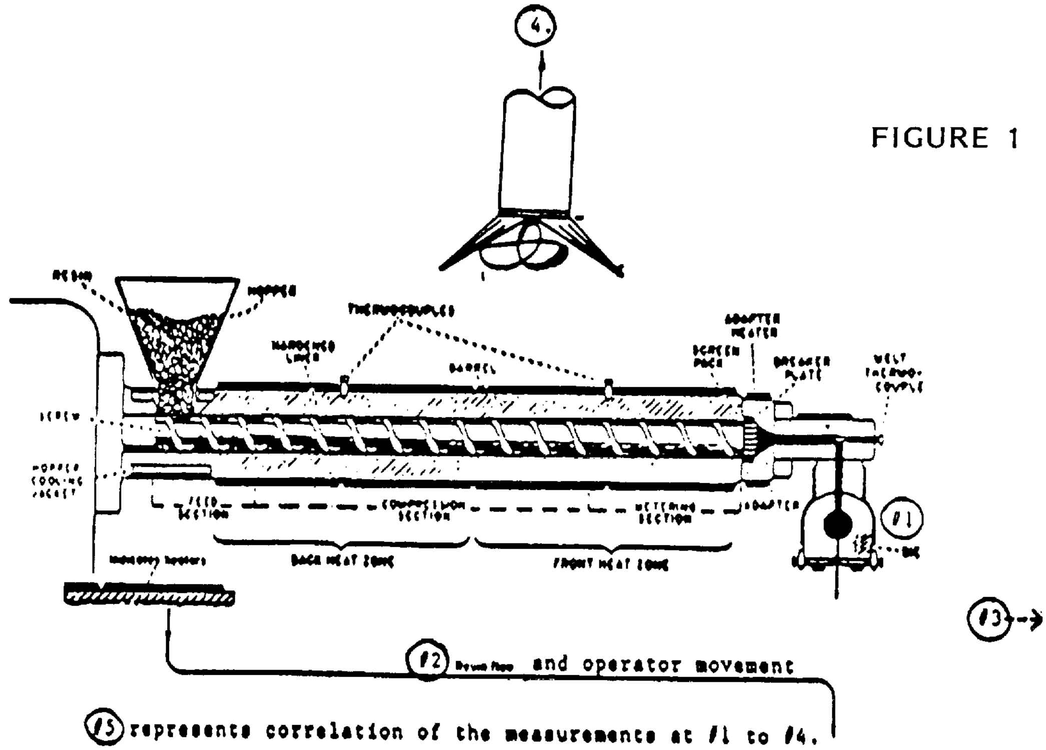
I. Relevance of plastics industry research to aerospace composites

At first view, plastics process emissions research may not seem to have much bearing on outgassing considerations relative to (advanced) composite materials, as discussed by other speakers in this session. We believe several parallel issues and cross-currents are of mutual interest, however, and that different perspectives among the audience will identify these for themselves. At the very least, many within the aerospace industry and NASA use plastics and fiberglass articles in non-structural roles. Familiarity with topically-driven research in those areas may prove useful within readers' organizations.

Figure 1 illustrates topics of concern to plastic processors in the context of "off-gassing" as that term is used on the shop floor. Compliance requirements range from observation of OSHA's Hazard Communications Standard, through TSCA, various industrial hygiene standards, to EPA's environmental regulations.

Today's summary is concerned only with the effort to quantify volatile organic compound (VOC) emissions within the meaning of Title I of the Clean Air Act, and the effort to characterize and quantify hazardous air pollutants (HAPs) within the meaning of Title III.

FIGURE 1



	Compliance pressure	Status	Research requirement	Other need	Priority
1. Thermal degradation products	HCS Prop. 65 TSCA	Not yet widely affecting processors	Not within scope of OHEIC: too varied, specific	Management educational information	Moderate
2. Operator exposure	OSHA 1910.1000 Part 6 b) rules	Current enforcement	NIOSH methods exist and accepted	Briefing from available sources	Moderate
3. Industrial area sample	Supplemental; STELs (?)	Occasional use	Not evident- adaptable from NIOSH, EPA	General guidance, case study examples	Low
4. Environmental emission	SIPs, Clean Air Act. Local ordinances.	Current problem for bsns formation. In future, more widespread.	EPA methods published, some may not apply.	Case method workshops on state usages. CAA compliance newsletter.	High for current applicants; will be high for many others later.
5. Correlations	Exclusions, exemptions, threshold determinations	A developing concern. techniques of high interest for post 1994.	Data and ratio gathering first. Testing later to fill gaps.	Validations: e.g., "low ppm at work station--no environmental emissions."	Moderate to 1994; High in '94-98 period

II. Impact of Clean Air Act Amendment Requirements

A new regime of Federal air quality laws are to be implemented this fall and early in 1995 by the states. Over 34,000 facilities which use chemical compounds will eventually be affected. Some local air pollution control districts have already begun to notify stationary sources of new filing requirements. There will be considerable variation between local requirements. Many manufacturers previously exempt from air pollution permits will now need to conduct measurements or otherwise secure data to determine how their state's rules apply to their facility. Even small air pollution sources will need to do considerable research to document that their activities are below the threshold of regulation.

The Society of the Plastics Industry (SPI) activities have concentrated on Titles I, III, and V of the Act. Title I, among other subjects, regulates volatile organic compound (VOC) emissions depending on a metropolitan area's ozone attainment status. Title III proposes regulation for 189 specific air toxics, listed as "hazardous air pollutants" (HAPs). Some HAPs are ozone precursors, and therefore potentially regulated under VOC provisions in Title I, as well as the HAP provisions of Title III. Styrene is an example. Title V of the Act describes minimum criteria for the states' air permit programs. Because of the unprecedented complexity of the permit process, SPI is very active with compliance alerts and as a guidance source on Title V.

In particular, students of the CAAA are following states' efforts to provide certain sources with means to "opt out" of the full Title V Permit process. This option is available to sources which are classified as "major" by their theoretical "potential to emit" but in fact have a much smaller release of tons per year of air pollutant.

Such sources can accept a "Federally-enforceable" (sometimes "FESOP") limitation such as a rule limiting volume of materials usage, a ceiling on their operating hours, or some other measurable limitation.

The intermittent or batch process nature of polymer composites production suggests that such "FESOPs" may be viable for many aerospace component producers. Others may need to identify MACT -- Maximum Achievable Control Technology -- for their process and build or retrofit their facility accordingly.

A full analysis of the CAAA, particularly MACT analyses, is beyond the scope of this presentation. But it was foreseen as early as 1989 that processors would need more refined tools simply to identify and quantify environmental emissions from their facilities, even before translating this information to permit applications and prior to considering process controls.

Unlike traditional permit programs, Title V puts the burden on the applicant -- not the regulatory agency -- to specify all applicable requirements, and to show how control strategies will be implemented and compliance will be proven. In addition to all applicable air-quality regulations (including those promulgated but not yet in effect), permit applications must describe products and processes produced at a site, and identify fuels and raw materials, pollution-control and monitoring devices, and data-collection procedures.

III. Scope of the Society of the Plastics Industry, Inc. activities

The Society of the Plastics Industry, Inc. (SPI) is the major national trade association for the U.S. plastics industry. SPI is comprised of more than 2000 member companies, representing approximately 75% of the dollar volume of plastics sales in the United States. SPI is organized to provide general "core" services which benefit all segments of the industry. But, reflecting the diversity of the use of plastics, it also operates units or committees organized along materials, process, or market lines. These committees include resin manufacturers, distributors, machinery manufacturers, plastics processors, model makers and other industry-related companies and individuals. Founded in 1937, SPI serves as the "voice" of the plastics industry.

A. Thermoplastic process emissions

1. University of Lowell research

Research was commissioned in 1991 by the Society of the Plastics Industry's (SPI) Occupational Health and Environmental Issues Committee (OHEIC) at the University of Lowell, Massachusetts. The objectives of this work were several: to establish a protocol for identifying and quantifying polymer off-gasses, and to ascertain whether there were constant ratios between off-gasses at the work station and emitted pollutants from the facility. The study is in the literature, as a poster paper given at the 1993 meeting of the American Industrial Hygiene Association: "Thermal Emission Identification of Organic Vapors Generated During Plastic Processes," C.W. Lu, R. Moure-Eraso, M.J. Ellenbecker, Department of Work

Environment; N.R. Schott, J.C. Huang, Department of Plastics Engineering Department, University of Massachusetts at Lowell, Lowell, MA 01864.

Organic vapors, and in some cases benzene soluble particulate (BSP) and total particulate, were sampled from the hot melt industrial processing of plastic and analyzed to measure vapor and particulate emissions. Organic vapor samples were collected on charcoal tubes and analyzed using gas chromatography/mass spectrometry. Four plastic processes were studied using industrial size machinery: injection molding, extrusion strand, extrusion sheet, and thermoforming. Nine organic vapor samples were taken six inches from the melted plastic output. Five particulate samples and five BSP samples were taken. Organic vapor samples were 2 to 6 liters, and particulate and BSP were 60 to 150 liters.

In the processing of medium-impact polystyrene, for example, nine major organic compounds were found, i.e., 1) benzene, 2) toluene, 3) acetophenone, 4) styrene, 5) benzaldehyde, 6) ethyl benzene, 7) alpha methyl styrene, 8) isopropyl benzene, 9) $C_{16}H_{12}$ isomer.

Percentages of organic compounds emitted were calculated by dividing the amount of each component by the total mass of all collected emissions. Emissions were detected for each plastic process cited above. The emissions actually sampled were a fraction of the total emitted since the conditions of industrial production preclude the stoichiometric capturing of all emissions at steady state. The focus of the study was the emissions generated by plastics processing at industrial operating temperatures. Emissions from additives or purging operations were beyond the scope of this study.

Essentially, this research effort became confused by the diversity of objectives, the discrepancy of interest between analytical chemists and industrial hygienists, and disagreement between the academic and industrial participants on how to simulate industrial production. The work was therefore useful in revealing the complexity of the off-gassing issue. It set the stage for more appropriately-controlled research elsewhere.

2. Polymer processing research at Battelle Institute

The unsuccessful work at Lowell moved supplier members of SPI's OHEIC to refine objectives and separate into task groups based on materials composition. Through proprietary research experience it was determined that facilities and expertise exists at the Battelle organization, Columbus, Ohio. Thus far polycarbonate, acrylonitrile butadiene styrene (ABS), and polyethylene resin systems have been evaluated. Nylon, polypropylene, and additional task groups are forming in line to have analysis performed through this facility, using appropriate variants of the basic protocol.

The fume generation facility at Battelle is used to generate and capture fumes produced during the processing of resins and composite resin systems. This facility was specifically designed to perform safety evaluations of fumes produced during plastic processing under controlled conditions which model industrial practice.

The program consisted of the following two phases: 1) development and validation of a fume sample collection and analysis method, and 2) collection and analysis of fumes emitted from selected production processes. The experimental design was developed by Battelle.

A method was developed which used stainless steel canisters treated by the Summa passivating process to collect the VOCs in fumes generated, for example, from the extrusion of ABS resins. The canister samples were analyzed concurrently by a gas chromatography system equipped with parallel flame ionization detection (FID) and mass selective detection (MSD). A similar method was successfully used in past studies characterizing aircraft engine emissions for the U.S. Air Force. (Aircraft Emissions Characterization from selected engines, Reports ESL TR 87-27 and 87-63 Tyndall AFB, Florida, March 1988. Available through NTIS.)

The characterization of process off-gasses in the Battelle research is comprehensive. Table I illustrates the range of compounds identified during the extrusion of ABS. Despite its complexity, the value of the work at Battelle is proving very practical for plastics processors. The research has documented that, in common production, 180 micrograms of VOC emission are generated for every gram of representative compound. In other words, a processor of 1 million pounds of ABS annually will emit only 180 pounds of VOCs, well below the threshold of regulation even in severe non-attainment zones. As to characterization, ethylbenzene was the largest component of the VOCs, with an emissions rate of 50 micrograms per gram of ABS.

The data indicates that a facility will process a great deal of this family of resin to reach any of the thresholds. A typical high-volume plastics processor, finding emission rates in the part-per-million range, will calculate to less than a ton of annual VOC emissions in this particular scenario.

Polyolefin manufacturers now have followed the ABS lead to calculate emissions rates, while Dow Chemical has calculated polystyrene emissions independently. Suppliers who have done such research are at a competitive advantage when they can supply emission rate data to processors applying for Clean Air Act permits.

3. Revision of EPA Manual AP-42

SPI OHEIC's research was given new impetus by a contract let from EPA's Office of Air Quality Planning and Standards in 1993. EPA selected contractor MRI Inc. to review the existing AP-42 Manual's chapter on plastics process emissions and propose a "Development of Test Strategies for Polymer Processing Emission Factors" if any gaps in the existing emission factor guidance were found.

SPI was dismayed to learn that EPA even tentatively considered using the 1985 AP-42 in the context of the Clean Air Act Amendments. The chapter in question is very faulty, based on lost references or a cursory and outdated study performed

TABLE 1

TARGET ANALYTES AND TENTATIVELY IDENTIFIED COMPOUNDS FOUND IN PHASE 1 AND 2 FUME (CANISTER) SAMPLES

Peak Number	Compound Name
1*	1,3-Butadiene
2*	Acrylonitrile
3*	4-Vinyl-1-Cyclohexene
4*	Ethylbenzene
5	m and p-Xylene
6*	Styrene
7	o-Xylene
8*	Isopropylbenzene
9	Benzaldehyde
10*	n-Propylbenzene
11*	Methyl styrene
12	1-Methyl-2-isopropylbenzene
13*	Acetophenone
14	p-Ethylstyrene
15	1-Methylene-4-isopropylene cyclohexane
16*	2-Phenyl-1-propanol

* Target analytes

in 1978 by a research organization which no longer exists. Moreover, MRI's subsequent report repeated unrealistically high emission factors, in the range of 2.1% to 7.5% by weight, for thermoplastics. And, it proposed using pyrolysis with gas chromatography/mass spectroscopy as a laboratory simulation of polymer processing. Thermogravimetric Analysis (TGA) technique was proposed as appropriate to conclude process emission evaluations. SPI believes this approach is seriously deficient for the purpose intended.

- Pyrolysis GC/MS provides for a brutal destruction of the polymer and does not reflect the changes in the polymer which occur during actual processing. GC/MS may provide data, but we suspect it is very different from what is seen in industrial processing. Relative surface area is likely to be much smaller and the hot air exposure time may be much shorter. Additionally, pyrolysis GC/MS would provide no shear of the polymer and potentially high oxygen levels versus high shear and low oxygen levels in, for example, an extruder.
- Typically, TGA methods involve heating the polymer sample from ambient to high temperatures at a fairly slow rate (e.g., 10°C/min). To achieve simulated polyethylene (PE) processing temperatures (e.g., 260°), a residence time of more than 20 minutes would be required. Normal PE processing residence times are on the order of seconds to a few minutes.
- The TGA measures only overall weight loss. If coupled with FTIR the data would give general qualitative identification of emissions. TGA should be used only to identify substances of potential interest.
- The TGA method is designed to measure weight loss at percentage levels versus traditional trapping industrial hygiene equipment which can routinely measure to ppm levels. Analysis of the trapped components also can be compound-specific.
- The TGA method may not duplicate actual atmospheric conditions during processing. Most thermal processing steps result in very low levels of entrained air. TGA analyses run under an inert atmosphere (e.g., nitrogen) may underestimate the emissions, while analyses run under an oxidative atmosphere (air or oxygen) would overestimate them. Researchers have commented on TGA data's showing "creation of matter."

SPI believes these methods are suitable, at best, for qualitative identification of process emission compounds. They cannot generate quantitative emission factors. For this phase of the technology, SPI recommends conducting pilot scale tests using conceptual emissions models. The development of such models to a reliable level, however, will arise from successive pilot studies, not laboratory research. In the final assessment of emissions, the information must be checked in actual plant situations.

Polymer structure (molecular weight, its distribution, degree of unsaturation, and catalyst residuals) will affect emission types and levels. In addition SPI processors have assembled a shopping list of variables affecting a given facility's emissions:

- humidity
- available air volume
- air movement
- mold release used
- condition of process equipment
- aerosol content
- additive content
- filter media
- polymers processed at adjacent equipment
- polymers structure
- molecular weight
- branching
- other reactive gas present
- its own volume/other gas' volume
- cleaning solvent present
- vapor pressure
- thermal history
- comonomer type and level
- compound purity

B. Reinforced plastics/composites process emissions

1. Pultrusion

Pultrusion processing of unsaturated polyester reinforced with continuous glass fiber is potentially a significant styrene emission source, to the extent that the glass passes through an open resin bath on its way to the shaping tool. Research by the Pultrusion Industry Council, a unit of SPI's Composites Institute has demonstrated that emissions at this work station are directly proportional to warm, unrestricted, airflow over wet surfaces. Re-engineering measures to minimize this feature of uncontrolled process emissions are relatively obvious in concept. The Council has recently joined with the SMC/BMC Environmental Committee described below to have an environmental engineering firm document MACT for the pultrusion process.

2. SMC/BMC emissions studies

The processing of sheet molding compound (SMC) and bulk molding compound (BMC) would appear at first glance to rank low as an emission source relative to other fiberglass composites manufacturing methods. Both prepreg-like materials are processed by closed molding methods, i.e. in compression presses or by injection molding. The mixing process, however, in which the resins are combined with fillers, pigments and other additives to make the "B-staged" molding compound can be a significant emissions source. SMC/BMC operations also tend to process relatively large amounts of material, since their major market by far is the automotive and light truck sector. Within the Composites Institute of SPI, an active SMC Environmental Subcommittee has shared within its membership the results of in-house emissions evaluation at members' own facilities. This group has also awarded a contract recently to an independent environmental engineering firm to perform an analysis of "Maximum Available Control Technology" (MACT) for their category of operation.

It might be mentioned here that SMC/BMC compounders and molders are high-volume users of VOC-generating cleaning solvents. While substitute cleaners are on the market, these do not appear capable of replacing aggressive solvents needed to clean molds and equipment where the contamination is out of line-of-sight or inaccessible to pressure cleaning. Recently a National Emission Standard for Hazardous Air Pollutants (NESHAP) has been published describing MACT for the aerospace industry using such cleaners. The technologies specified appear to have transfer value to other industries.

3. "Open molding" processing: CFA styrene emissions protocol

Another research project should be brought to your attention, if for no other reason than its appearance in future databases as a "composites" study. The research has additional relevance to the polymer composites audience in the event interest groups wish to undertake emissions testing which will be submitted to EPA. The agency has high interest in monitoring the quality of such research, and cannot be counted on to accept it outright. In fact, it is possible that industry or academic-initiated research, when intended to establish a protocol, may not be acceptable to EPA if it does not follow EPA's Quality Assurance procedures.

This test method development program is initiated by the Composites Fabricators Association. CFA is the trade association, with over 700 member companies, which serves the interests of small manufacturers who typically process unsaturated polyester or epoxy vinyl ester resins reinforced with glass fibers. (More of these companies are beginning to handle "advanced" materials, and certain advanced composites molders have joined CFA for its small-business program benefits.) CFA fabricators normally supply the recreational boating industry, the automotive and heavy truck aftermarkets, and both the residential and architectural construction industries. They are present as suppliers to general aviation, and as builders of prototypes and short-run orders for the commercial aircraft market as well.

CFA's program is driven by current state regulators' demands for Reasonably Available Control Technology (RACT) assessments. Also, the development of the Clean Air Act Amendment (CAAA) regulations, and in particular the Maximum Available Control Technology (MACT) standards for the reinforced plastic composites industry, will require definitive baseline data on styrene emissions from the open molding process.

The purpose of the CFA/EPA study is to measure styrene emissions from polyester resin spray application, polyester gel coat spray application and resin hand batch application. The accurate characterization of styrene emissions from this project will establish a background for subsequent studies, which will explore emissions reduction methods. Faulty conclusions from this study may lead to incorrect methods of addressing emissions reduction in subsequent studies. Therefore, a comprehensive Quality Assurance Plan will be in effect to support the testing program.

Investigations of available literature reveal that styrene emissions testing which has been done in the field presents an erratic and unacceptable range of results, which may be due to the uncontrolled environments in which the studies were conducted. This study will control environmental variables in order to isolate baseline emissions from the process.

The Process and Test Facility

The open molding application methods included in this experiment are polyester resin spray application, polyester gel coat spray application and polyester resin hand batch application. The testing will be carried out at the Dow Chemical Composites Laboratory in Freeport, Texas. The test area is a 10' X 14" exhaust hood. Natural draft openings (NDO's) are arranged in accordance with EPA Method 204. See attached Sketch No. 1.

Airflow in the temporary enclosure will be maintained at 1500 cfm and ambient air temperature will maintained at 70°F. Sampling ports will be located in the exhaust duct. A three-sided mold of 30 ft^2 will be located in the center of the test enclosure at a height of 1 ft. above the ground.

The design of this experiment is intended to fulfill the requirements of a USEPA Category II Quality Assurance Project Plan (QAPP). The purpose of the Category II QA Project Plan is to present the data generated to the USEPA in an acceptable and standard format, in addition to maintaining a high confidence level in the development and handling of data.

This program is planned with a pretrial to verify the design of the experiment and to debug the emissions measurement procedures. Some of the details of the experiment may be altered as a result of the pretrial, however the basic protocol will remain the same.

Preliminary results are expected about November 1. The experiments and development of the procedure are likely to be discussed in both an EPA Control Technology Guideline, and in a monograph for the Air and Waste Management Association proceedings.

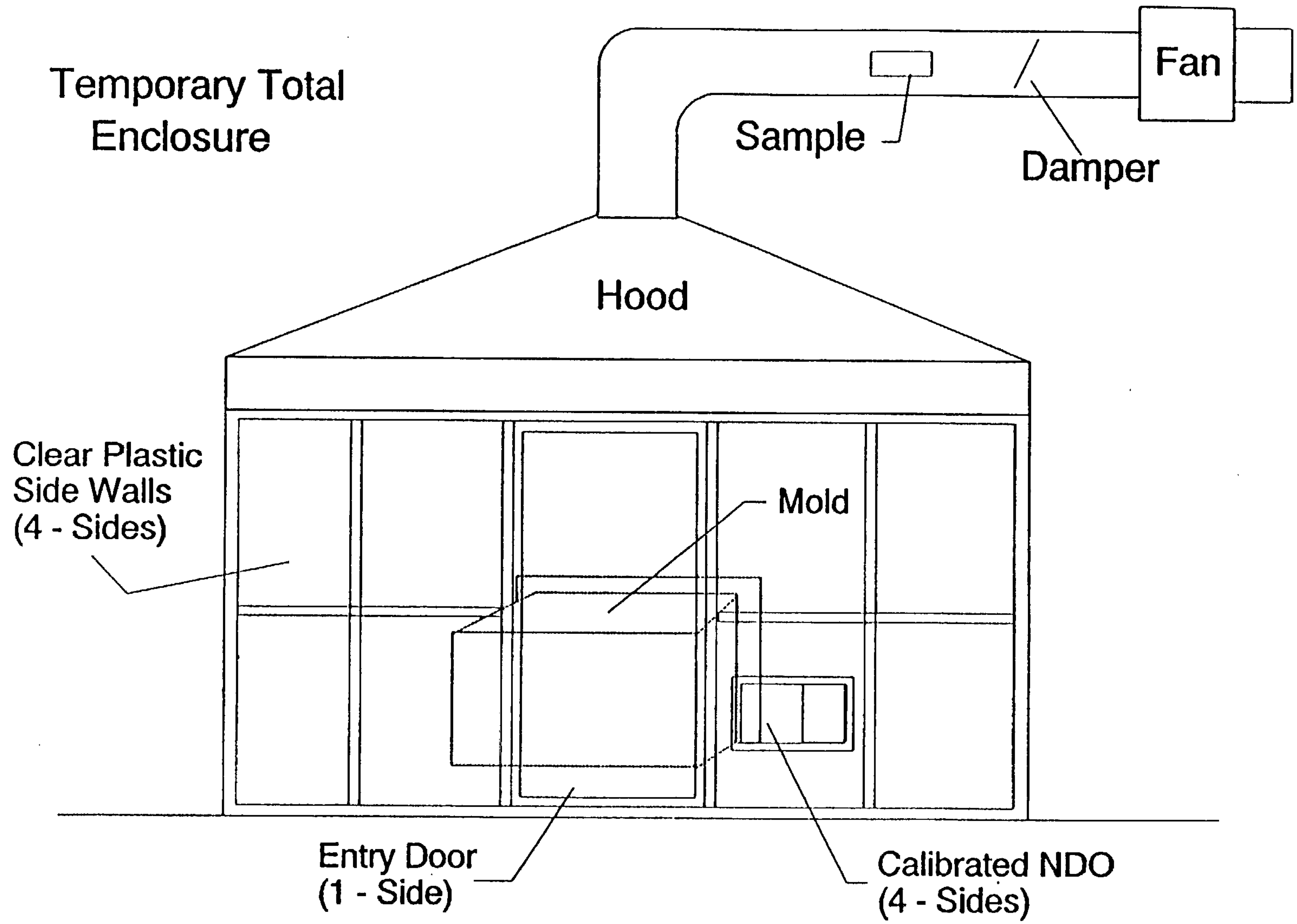
Emissions measurements will be made using both active and passive sampling. A Varian 3700 gas chromatograph, equipped with a flame ionization detector will be used. Passive dosimeter badges will be used in conjunction with the active sampling of the GC. These 3M brand passive dosimeters will be analyzed by the Dow Industrial Hygiene Services laboratory. Mass balance calculations will be made using all material input weights, minus cured test panel weight.

Statement of Project Objectives

The project objective is to measure baseline styrene emissions from the open molding process. Air temperature and air flow will be held constant throughout the modified Taguchi experiments, to reduce environmental influences on emissions. The process will include resin spray application, gel coat spray application and resin hand batch application. The methods, materials and equipment used will represent a typical set of parameters commonly found in the FRP composites industry. In the Phase I study no attempt will be made to reduce styrene emissions.

Thermoset resin emissions

For survey completeness, it may be mentioned that the Epoxy Resin Systems Group of the SPI is developing information to establish a MACT NESHAP for liquid epoxy wet strength resins. At this time the scope of this research is the assessment of air toxics from the resin production facilities. It remains to be seen whether this activity will generate information useful to prepreggers and molding/fabrication users of epoxy compounds and prepregs.



SKETCH No. 1

11A

IV. Utility of SPI research for advanced polymer composites audience

Users of chemical compounds, including wet resins and advanced polymer composite prepregs, may be regulated under various provisions of the Clean Air Act Amendments of 1990. Resin producers are normally familiar with the intricacies of air pollution permit requirements, but small compounders, prepreg manufacturers and contract molders, and the polymer composite production shops of aerospace OEMs, will need to evaluate whether they are in the regulated community. This determination, and the generation of environmental emissions data for permit applications, is not easily completed. The numerous variables inherent in producing composite articles make it difficult for suppliers to provide users with useful emission factors valid for specific operating scenarios.

Research by polymer suppliers through their national trade association, SPI and its several operating units, has begun to sort out the complexities of production analysis. SPI has demonstrated that laboratory analysis by familiar analytical chemistry methods is not appropriate either for the identification or quantification of environmental air emissions from industrial processes which use polymer materials. SPI recommends well-designed process simulations, at as full a scale as possible to actual production conditions, and then verification of pilot-scale results under production conditions specific to the operator's practice.

EPA and the State Implementation Plans (SIPs) it approves will not necessarily accept industry-generated emission data from non-standard research demonstrations. Trade or industry-specific coalitions should work with EPA's research offices at Research Triangle Park, NC to pre-quality such experiments. This step, while time-consuming, will facilitate adoption of industry evaluations into EPA Control Technology Guidelines in the case of VOC control, and NESHAPs in cases where MACT demonstration is required.

Aerospace end-users of composites who do not themselves manufacture these goods have a stake in monitoring their sources of supply to determine that they are prepared to generate data for all permits which will be required.